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Evaluation of Salt Removal from Azulejo Tiles and Mortars Using Electrodesalination

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ABSTRACT

Azulejo tiles are part of the Portuguese cultural heritage and are worldwide appreciated. The durability of this building material is affected by the accumulation of salts, causing fractures and peeling of the glazing and ultimately leading to the degradation of the tile panels and the irremediable loss of historic value. In this work preliminary studies with single tiles presenting an underlying layer of mortar have been conducted to assess the amount of salts that can be removed from the building material using a new technique called “electrodesalination”, in which the salt’s ions are transported out from the tiles by applying an electric current on the backside.

Results shown here include an assessment of how much of the salts did come out in comparison to what was originally there, and additionally if the electrodesalination succeeded in removing salts down to a point where the tile and underlying mortar are no longer at risk of salt induced decay.

The main conclusions are that the technique is successful in extracting salts from mortars (removals efficiencies between 88% and 92%) but not as good for the tile (removals between 10% and 80%). The risk of salt damage to the mortar and tile was either considerably reduced or disappeared, except for one situation with nitrates, thus showing that even though some optimisation is needed, electrodesalination stands as a promising in-situ technique to improve durability of the historic valuable Portuguese Azulejo tile.

KEYWORDS

Azulejo, Salt removal, Electrokinetic

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1 INTRODUCTION

Azulejo tiles are part of the Portuguese cultural heritage and are worldwide. The durability of this building material is affected both by the original materials used and by the environmental conditions. The appearance of salts at the surface damages the tile (fractures, peeling, granular disintegration, etc.) and ultimately leads to the degradation of the tile panels, with the loss of historic value. Electrodesalination, also called electrokinetic extraction of salts, is a method under development which is based on well-established electrochemical principles: under the electric field positive ions move towards negative electrodes and negative ions move towards positive electrodes. As time passes ions will be depleted from the tile and concentrate in the vicinity of the electrodes (more detailed information about the technique can be found in Ottosen *et al.* 2010). One important advantage of electrodesalination compared to traditional poulticing (next to offering a faster transport of salts out from the material) is that the poultice with electrodes does not have to cover the whole surface to be desalinated. The electric field will be strongest where the conductivity is highest and that is where the ionic concentration is highest. Thus the electric field will be strongest exactly where the salts are concentrated even though the electrodes are not placed directly in this place.

Electrodesalination has been applied with success to single bricks (99% removal of NaCl; Ottosen & Rorig-Dalgaard 2009) and in a pilot scale experiment of a salt contaminated masonry from an old house (Ottosen *et al.* 2008). In a preliminary study on the desalination of Portuguese Azulejo tiles (Ottosen *et al.* 2010) significant decreases in salt content ($>81\%$ Cl^- , 59% NO_3^- , 22% SO_4^{2-}) were reported for single tiles without an underlying layer of mortar. However, in real situations the tile is usually applied to a wall with a layer of mortar, and this can affect the success of the desalination process. In the work presented in this paper the investigation was taken a step further by performing desalination on tiles which have an original underlying layer of mortar.

2 EXPERIMENTAL

2.1 Tiles

Azulejo tiles from 3 different epochs were used in the current work (see Fig. 1). A piece of tile (8x 6 x 1,5 cm) from the **XVII-century** was collected from the Alentejo region (south and central Portugal) and presents a yellow biscuit with white and blue glazing on the surface. On the backside there is a layer of mortar approximately 1.5-2 cm thick. A reference sample was obtained by cutting off a small piece from the corner.

The tile from the **XVIII-century** was removed from Palacio Centeno (in Lisbon) during renovation works due to severe salt damage. The biscuit is yellow, and measures 14 cm by 14 cm and is 0.9 cm thick. On the backside there is a layer of mortar between 0 and 1.5 cm thick. The mortar easily disintegrated and felt like coarse-grained sand. A reference sample was taken by cutting off a small piece from the corner.

The tile from the **XX-century** presents a red biscuit with dimensions 14cm x 14 cm x 1.5 cm. On the backside there is a 1 cm thick layer of mortar. Approximately one third of the surface is covered by a yellow and white glazing. One of the 2 tiles available was used as reference and the other was used in the electrodesalination experiments. The tile used as reference was segmented into 8 pieces: 4 used as reference for the mortar and 4 as reference for the biscuit.

2.2 Electrokinetic Desalination Experiments

The tiles had been stored in a box at room temperature and were almost dry, so before the experiments they were wetted by spraying distilled water on the back (mortar side) until the tile would not absorb any more water. For the experiment the tiles were wrapped in plastic film (to

prevent evaporation) and placed with the glazing facing down. Two square holes (3x3 cm, each) were cut in the upper surface of the plastic film, as far apart as possible. A plastic frame (approximately 4 cm high) was placed over each hole and filled with a poultice (mixture of kaolin and CaCO_3). An inert electrode mesh was placed over the poultice and covered with another thin layer of poultice. Plastic film was wrapped around these and the electrode mesh was connected to a power supply.

At the beginning of the desalination experiments the current was set to 5 mA and the voltage was around 20V. During the experiments the voltage was read once or twice a day (except for weekends) and the current was kept constant as long as the voltage did not increase more than 137 V. If the voltage was too low and remained unchanged for the following days then the current would be increased manually to a maximum of 20 - 25 mA (depending on the voltage).

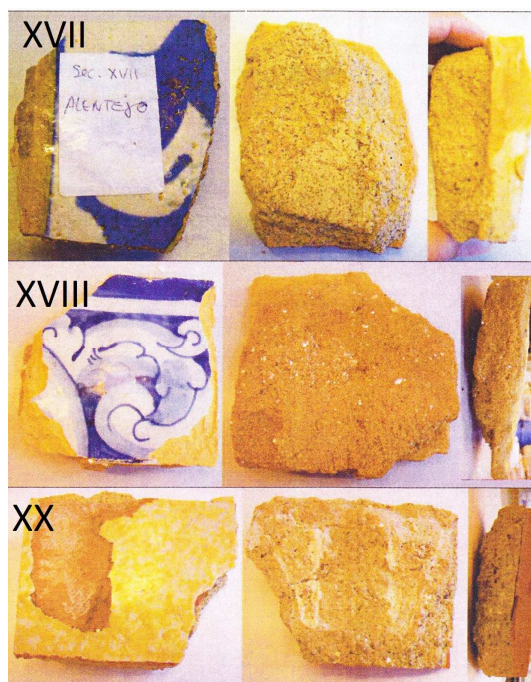


Figure 1. Photographs of Azulejo tiles used in the electrodesalination experiments (left: front of tile; middle: back of tile, with mortar; right: side view)

The poultice consistency was checked regularly to prevent drying. For the XX-century tile small amounts of distilled water were added to the poultice whenever it was too dry. However, fearing that this might flush salts that had been previously removed, it was decided to instead change the poultice (which occurred around day 23 of the experiment). Poultice for the XVIII-century experiment was initially changed once a week. After increasing the current, first to 10 mA and then to 20 mA, it was decided to change the poultice twice a week since at these higher currents acid production increases. The XVII-century experience lasted for seven days, so poultice was collected only at the end. Table 1 summarises the experimental conditions.

Table 1. Current, voltage and duration in the tile electrodesalination experiments.

	<i>XVII</i>	<i>XVIII</i>	<i>XX</i>
<i>Current</i> [mA]	1,51 → 0,47	4,99 → 10 → 20	4,99 → 0,99 → 0,54
<i>Voltage</i> [V]	20,7 - 75,0	2,4 - 31,8	13,7 - 91,7
<i>Duration</i> [days]	7	24	34

After the experiments the tiles were unwrapped and segmented into pieces (mortar and biscuit) with a hammer and a chisel, as depicted in Figs. 2 to 4. Segments were numbered from 1 to 3/4, with an anode placed over segment 1.

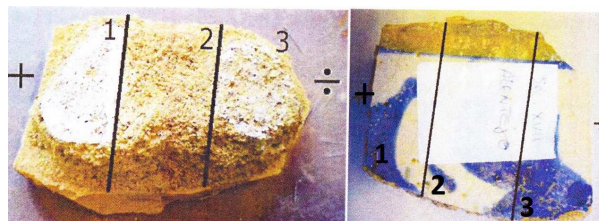


Figure 2. XVII-century. Left: segmentation of mortar; right: segmentation of biscuit.

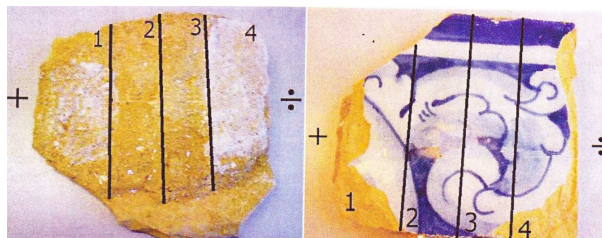


Figure 3. XVIII-century. Left: segmentation of mortar; right: segmentation of biscuit.

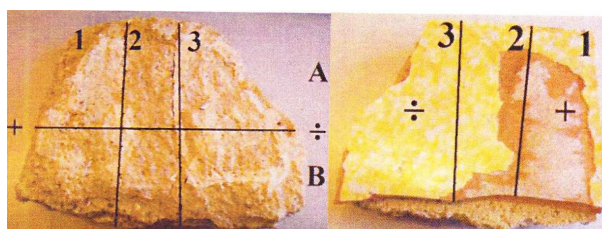


Figure 4. XX-century. Left: segmentation of mortar; right: segmentation of biscuit.

2.3 Analytical

Each segment (including references taken before the desalination experiments) was weighed, dried at 105°C for 24h and weighed again to determine water content. The dried pieces were then powdered by hand using a mortar and pestle. Extractions in distilled water (10g powdered tile suspended in 25 mL) were made and after 24-h agitation the pH was measured with a pH electrode and conductivity with a conductivity electrode directly in the suspension; the suspension was subsequently filtered and the concentrations of Cl^- , NO_3^- , SO_4^{2-} measured by ion chromatography and Na^+ by atomic absorption.

3 RESULTS AND DISCUSSION

This investigation includes 3 electro-desalination experiments, each conducted with a tile from a different epoch: XVII-century, XVIII-century and XX-century.

3.1 Biscuit and Mortar Characterization

Values for conductivity, pH and ion concentrations measured in the different biscuits and mortars are shown in Table 2. These values were measured on reference samples taken before the electrodesalination experiments. For the XX-century tile 4 fragments were used, whereas for the other epochs only one sample was analysed, which consisted in a small piece taken from the corner of the tile. Standard deviation in the XX-century reference shows a high variability for salt concentrations, indicating that biscuit and mortar are not homogeneous. This variation is more generally related to the salinization process than to the composition of the original base materials. When water evaporates at the surface of the tile leaving the salts behind (one of the possible salinization processes) it draws more water and salts from the surrounding materials (wall and ground) by capillary forces. The tile surface is covered with an impermeable glazing and water either evaporates at the joints (between the

tiles) or through cracks in the glazing. This means that water channels are formed within the biscuit and that the spatial distribution of salt is highly variable: i.e., a sample taken from a particular spot might not have salts at all, whereas another taken 2 or 3 mm away might have singular amounts. As a consequence, it is important to note that reference values for XVII and XVIII century tiles, which are based on a single, small sample taken from the corner of the tile before electrodesalination might not in any case be representative of the entire specimen.

To evaluate the initial anion concentrations in the tiles and mortars (shown in Table 2) comparison is made with the Austrian Önorm B3355-1 “Dehumidification of masonry – Building diagnostics and planning principles”. This standard gives two thresholds (see Table 2): If the concentration is below the lowest threshold there is no risk; if the concentration exceeds the highest threshold, active salt removal is advised; in between the two thresholds values an individual, specific evaluation must be performed. Additionally to this standard classification the authors use the expression “severe problem” whenever the salt concentration is at least 4 times higher than the upper threshold value.

Table 2. Reference values for tiles and mortars (before experiments).

<i>Century</i>	<i>No. of samples</i>	<i>pH</i>	<i>Conductivity</i> [mS/cm]	<i>Cl⁻</i> [mg/kg]	<i>NO₃⁻</i> [mg/kg]	<i>SO₄²⁻</i> [mg/kg]	<i>Na⁺</i> [mg/kg]
XVII mortar	1	9,0	0,31	93	126	32	41
XVII biscuit	1	9,1	0,26	53	42	53	53
XVIII mortar	1	8,9	15,07	6656	13921	64	3480
XVIII biscuit	1	8,2	17,61	7927	17036	350	4680
XX mortar	4	9,5±0,1	1,28±0,89	222±111	133±62	1542±1493	47±18
XX biscuit	4	9,6±0,2	0,59±0,39	78±18	39±24	653±585	38±7
Önorm B3355-1 (Thresholds)	Low:	-	-	300	500	1000	-
	High:	-	-	1000	1500	2500	-

The concentrations of Cl^- , NO_3^- and Na^+ in the XVIII-century tile are very high, largely exceeding Cl^- and NO_3^- upper threshold values, thus indicating a severe salt problem. The panel from where this tile was collected showed visible signs of salt damage, and high salt concentrations were expected.

For the XX-century tile concentrations of SO_4^{2-} lays between the two thresholds of values given in the B3355-1 standard, indicating that this ion might cause problems. Concentrations of other anions are below the lower threshold and therefore do not constitute a problem.

The XVII-century tile had comparatively small amounts of salts, all lying well below the lowest threshold of the B3355-1 standard. According to these results, summarised in Table 3, there are 3 situations where desalination is required or advisable, namely: removal of Cl^- and NO_3^- from the XVIII-century tile and removal of SO_4^{2-} from the XX-century tile.

3.2 Desalination Results

Discussion of electrodesalination results of the 3 tiles will focus on the situations where salts are a problem, namely Cl^- and NO_3^- from the XVIII-century tile and SO_4^{2-} from the XX-century tile. The sections under this heading include (1) concentration profiles of salt in mortar and biscuit after desalination; (2) removal efficiencies; and (3) evaluation of final salt concentrations.

3.2.1 Profiles after the desalination

The reference analysis of the **XVIII-century** tile indicated that it had a severe salt problem, with concentrations of Cl^- , NO_3^- and Na^+ reaching several thousand mg/kg. After being submitted to electrodesalination for 24 days the concentrations in the mortar were considerably reduced (Fig. 5) for all ions but SO_4^{2-} , whose initial concentrations were already low (<100mg/kg). The concentrations were also decreased in the biscuit. Ion concentration varies in the 4 segments, forming a typical

profile: as the ions move towards the target electrodes through the segments they become depleted in the segment from which they migrated and accumulate in the next segment. The results shown in Fig.5 are consistent with ion's charge: negative ions (Cl^- and NO_3^-) move under the electric field towards the anode (target electrode) placed over segment 1, resulting in lower concentrations in segment 4, while the positive ion (Na^+) moves towards the cathode placed over segment 4, with concentrations being minimum in segment 1. Accumulation of ions near the target electrode means that the desalination is not yet completed, and that ions are still moving from the segment into the poultice. As opposed to the differentiated profiles obtained for Cl^- , NO_3^- and Na^+ , it can be seen that SO_4^{2-} concentrations are approximately even in the 4 segments, probably meaning that all mobile molecules under the electric field were removed, and only a residual, non-mobile fraction remains. The **XX-century** tile has high initial concentrations of SO_4^{2-} , which decreases considerably after the 34-day electrodesalination experiment (for both tile and mortar). Residual values are similar in the three slices, indicating that all mobile SO_4^{2-} has been removed (Fig.6).

Table 3. Recommendations for the different materials according to their ion-concentrations

<i>Tile/Mortar</i>	<i>Cl</i>	<i>NO₃⁻</i>	<i>SO₄²⁻</i>	<i>Recommendation</i>
XVII-century	No problem	No problem	No problem	No action required
XVIII-century	Severe problem	Severe problem	No problem	Desalinization is required to remove Cl^- and NO_3^-
XX-century	No problem	No problem	Might be a problem	Desalinization might be advisable to remove SO_4^{2-}

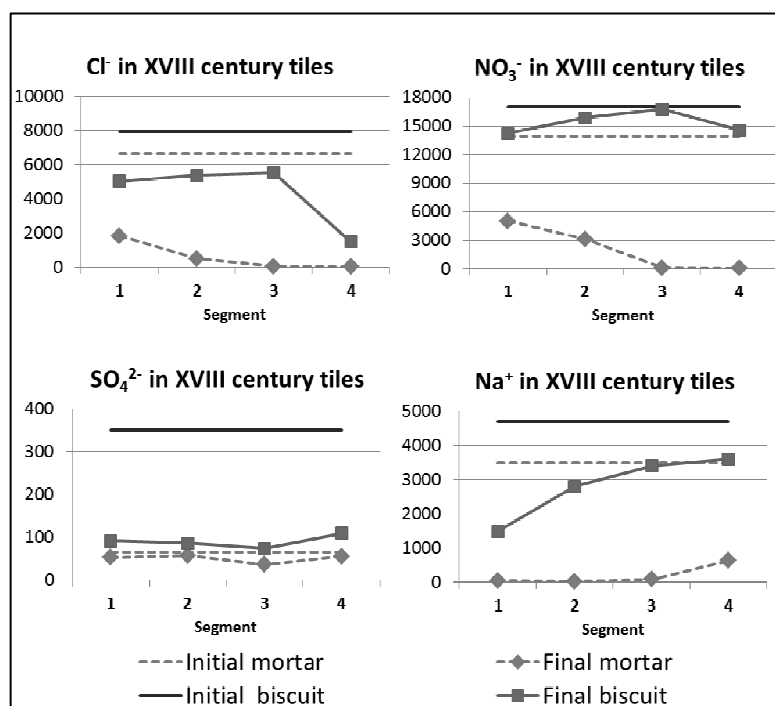


Figure 5. Concentration profiles (mg/kg) of Cl^- , NO_3^- , SO_4^{2-} and Na^+ in mortar and biscuit of XVIII-century tiles after electrodesalination

3.2.2 Removal efficiency

This section estimates how many ions the electrodesalination process was able to remove from the building materials as a percentage of what was originally there. Removal efficiencies are shown in Fig. 7 for the previously identified situations. When looking at these results one must keep in mind that they are based on an assessment of the initial concentrations which might not be representative of the tile, as was previously discussed (section 3.1).

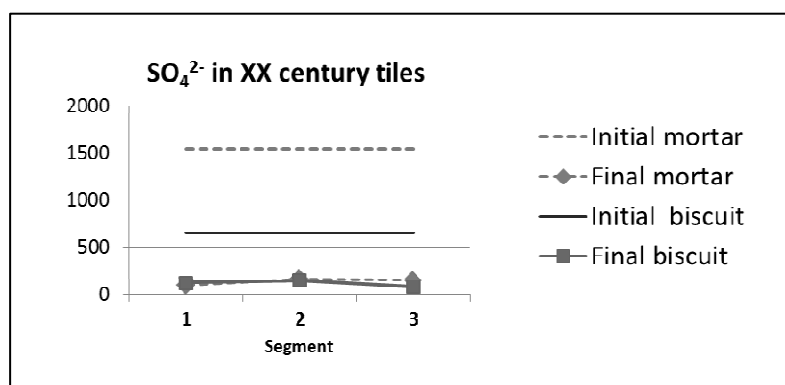


Figure 6. Concentration profiles (mg/kg) of SO_4^{2-} in mortar and biscuit of XX-century tiles after electrodesalination

Figure 7 shows that removal of ions from the mortar was very successful, with efficiencies between 88% and 92%. Biscuit desalination was not as good, with efficiencies ranging from 10% to 84%.

Why the biscuit seems to be more difficult to desalinate than the mortar can only be hypothesized at this point, but possible explanations range from the lay-out selected (electrodes are placed on mortar side, to physical characteristics (porosity, water content, chemical form of salts) all of which influence the solubility and mobility of the ions.

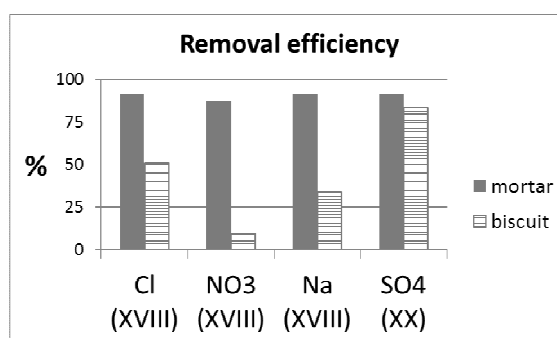


Figure 7. Removal efficiencies for different building materials (mortar and biscuit)

By analysing the results so far it has been possible to establish the amount of salts removed from the building materials into the poultice, and to show how much that is compared to what was originally there. But is it enough? Did the electrodesalination succeed in removing salts down to a point where the tile and underlying mortar are no longer at risk of being damaged due to high salt content? In the following section the success of the desalination experiments is further evaluated by comparing final concentrations in the building materials with the absolute values given in the B3355-1 standard.

3.2.3 Final concentrations in the biscuit/mortar against standard B3355-1

In this section the electrodesalination is further evaluated by comparing final concentrations in the building material against the values given in the B3355-1 standard. The concentrations given in the standard can be discussed as they are developed for single salts, which we do not have in the experimental tiles, but these are the only limiting values which are given and thus they are used for the evaluation.

On the basis of the initial assessment of salt levels in the building materials, three situations have been previously identified as requiring some type of action. Salt levels after the electrodesalination are now represented together with the upper and lower thresholds given in standard B3355-1 (Fig. 8) and an update of the salt problem after desalination is presented in Table 4.

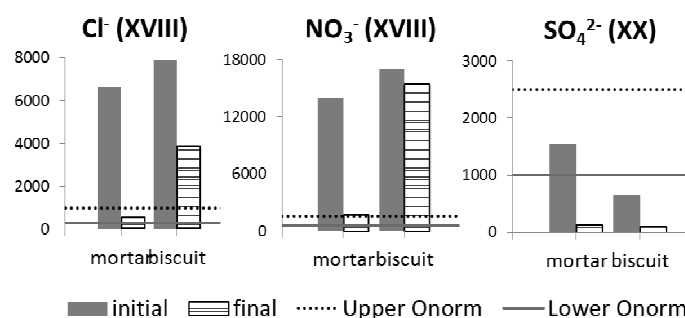


Figure 8. Comparison of initial and final levels of Cl^- , NO_3^- , SO_4^{2-} (mg/Kg) in mortar and biscuit with the thresholds of Austrian standard B3355-1.

From Fig. 8 and Table 4 it can be seen that mortar concentration were successfully lowered to either “no problem” or “possible problem”. Results for the biscuit were not as good: NO_3^- continued to pose a severe problem (even though considerable amounts of NO_3^- were removed) and Cl^- concentrations are still several times higher than the upper threshold of the norm.

Table 4. Update of salt problems after electrodesalination

		Cl^-	NO_3^-	SO_4^{2-}	Problem
		Before → after	Before → after	Before → after	solved?
XVIII	Mortar	Severe → possible problem	Severe → possible problem	-	MAYBE
	Biscuit	Severe → Problem	Severe → Severe	-	NO
XX	Mortar	-	-	possible → no problem	YES

4 CONCLUSION

Salts removal from the mortar adjacent to single tiles was very successful, with efficiencies ranging from 88% to 92%. Results were not as good for the biscuit, since salts were only slightly removed (efficiencies between 10% and 84%). This work shows that electrodesalination is a promising technique to desalinate mortar (and eventually the wall behind), but it still needs to be optimised to desalinate the tile. Further work will be conducted to solve the issues raised so that the technique can be applied in future restoration of the historically valuable Portuguese tile.

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